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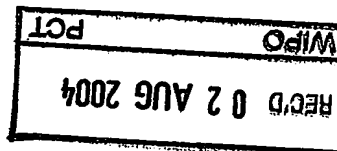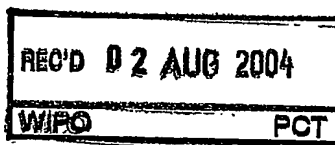
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PROVISIONAL APPLICATION FOR PATENT COVER SHEET

This is a request for filing a PROVISIONAL APPLICATION FOR PATENT under 37 CFR 1.53(c).

Express Mail Label No.	EU918147955US

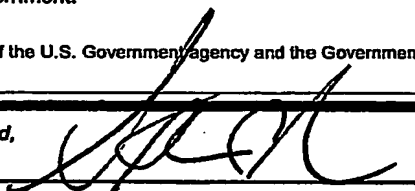## INVENTOR(S)

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☐ *Additional inventors are being named on the _____ separately numbered sheets attached hereto*

TITLE OF THE INVENTION (500 characters max)

REDUCED COST FLEXIBLE FUEL, METHANOL CAPABLE FUEL CELL AND COMPONENTS

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ENCLOSED APPLICATION PARTS (check all that apply)

☑ Specification *Number of Pages* **28**

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☐ Application Data Sheet. See 37 CFR 1.76

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☐ Other (specify)

METHOD OF PAYMENT OF FILING FEES FOR THIS PROVISIONAL APPLICATION FOR PATENT

☑ Applicant claims small entity status. See 37 CFR 1.27.

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The invention was made by an agency of the United States Government or under a contract with an agency of the United States Government.

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Respectfully submitted,

SIGNATURE _____

Date | 09/03/2003

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REGISTRATION NO. (if appropriate) | 27,591

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USE ONLY FOR FILING A PROVISIONAL APPLICATION FOR PATENT

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

PROVISIONAL PATENT APPLICATION
35 U.S.C. § 111(b)

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Title

        REDUCED COST FLEXIBLE FUEL, METHANOL
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REDUCED COST FLEXIBLE FUEL, METHANOL CAPABLE FUEL CELL AND COMPONENTS

Disclosed herein are improved designs for a methanol capable fuel cell electrode with reduced catalytic loading requirement, greater efficiency and means to refresh itself from poisoning.

This application further elucidates design permutations that fall within the descriptions and/or spirit of the inventions already disclosed in my U.S. Provisional Application Serial No. 60/464,874, filed April 22, 2003, titled (as amended) "REDUCED COST, FLEXIBLE FUEL, METHANOL CAPABLE FUEL CELL AND COMPONENTS." An embodiment disclosed in the fuel cell electrodes section of that application included a thin film catalyst applied to a porous type structure, adapted to allow fluid to flow through therein, with design considerations to make the unit substantially electrically conductive with a low internal resistance compared with the current art direct methanol, and PEM designs. There are many permutations of substances that can make up the porous sub-structure of the anode within the spirit of the invention. Several of them are described herein.

Background of the invention

Fuel cell technology has extraordinary potential, not just economically, but also to supply our power and transportation needs while drastically reducing global pollution. However, it is a nascent technology with several serious obstacles yet to overcome. These obstacles as yet have precluded extensive market viability. The first obstacle has been cost. While the materials and manufacturing costs are dropping at a rapid clip, most fuel cell technologies are, as yet, three to ten times more expensive than the technologies with which they compete. Cost has kept fuel cells to niche, "low hanging fruit" applications so far. The cost overruns are attributable to multiple components and systems as well as lack of scale economy.

A large part of the cost and size of the fuel cell stack is attributed to the expensive and bulky field flow plates and diffusion layers. In many systems, these parts account for the majority of the stacks cost, size and weight. A fuel cell with electrodes that can operate without these components will be considerably smaller, more efficient, less expensive and will have a much higher power density.

A second area of the technology needs further cost reductions is the inefficient usage of platinum. While tremendous strides have been made, fuel cells still rely on amounts of platinum that preclude mass production. Platinum is supply is so restricted that if the current art fuel cells were to go into mass production the platinum supply and demand curves would shift, prohibitively raising the price of platinum. Platinum is also an extremely environmentally damaging metal to obtain. Ten tons of earth are removed for every one once of platinum obtained. As discussed herein, the vast majority of the platinum in especially current art methanol powered fuel cells is wasted. Technology that that further reduces the electrode's platinum requirements could remove one of the barriers to fuel cell mass production by decreasing costs in three ways. There would be decreased costs of the required platinum per unit, the deleterious supply/demand shift

would be mitigated, and the additional cost savings of scale economics would be achievable.

The third obstacle to many forms of fuel cells is the current art's sensitivity to contaminants, which poison the electrodes and degrade the electrolytes, seriously limiting cell lifespan. Compounding this problem is that two of the most worrisome poisons are ubiquitous parts of petroleum fuel stocks and of air pollution. The levels of sulfur compounds and carbon monoxide from these sources shortness the fuel cells life span by progressively degrading its efficiency. Making this matter worse is that fuel cell intermediary reaction products can poison the electrodes and or electrolytes. There is tremendous research being done on many fronts to solve this problem. Currently, especially the lower temperature fuel cells require expensive and bulky fuel reformers, shift reactors, nannofiltraition units etc which add considerably to the size and prohibitive cost of the fuel cell system.

Another related obstacle facing fuel cells is the prohibitive cost, size and complexity of the 'balance of plant' apparatus. This is the necessary ancillary equipment required to operate a fuel cell stack. While the fuel cell stack has evolved into a simple compact design, it relies on extensive, costly supporting apparatus termed the 'balance of plant.' The balance of plant equipment is several times larger and often much more expensive than the fuel cell stack itself. A good deal of this equipment is necessary to mitigate the above current electrode's shortcomings. For most applications, it is the expense of the balance of plant apparatus that prices the unit outside of commercial viability.

The forth obstacle to broad commercialization of fuel cells is two categories of efficiency losses inherent to the current designs. (This, as most of what is put forth here is especially true for the lower temperature fuel cells.)

Electrical inefficiency: Current electrodes suffer from high internal resistance and impedance losses inherent to their make up. In the current art, the electricity must travel though a noncontiguous substrate of adhered, but not bonded carbon particles. This causes significant internal resistance and impedance losses. The problem is intensified in that the glue holding the carbon together is a very poor electrical conductor. These efficiency losses create the need for the expensive and bulky field flow plates that double as current collectors. However, in addition to the size and cost of these components, they also contribute their own efficiency losses from internal resistance and impedance.

Concentration gradient and diffusion efficiency losses: The vast majority of existing fuel cells pass the fuel stream by a diffusion layer longitudinally by the anode. The fuel diffuses across and into the anode. This is a rate limiting process and has several inherent other inefficiencies. Inert compounds and products can commonly become trapped in the spaces of the electrode and the diffusion layer mechanically slowing the ingress of fuel and decreasing catalyst utilization efficiency. These systems are highly sensitive to the amount of water in the microenvironment. However, the fuel cell essentially never achieve optimal water balance across all the stack components creating another efficiency loss.

The last major problem plaguing the industry is hydrogen. Hydrogen, a chemically ideal fuel, is prohibitively expensive and dangerous, and lacks the infrastructure for broad use. While it is clear to those in the field that someday there will exist cost effective and safe ways of producing, distributing and storing hydrogen, the

current lack of that technology impedes fuel cell commercialization. Hydrogen makes metal brittle, escapes through microscopic cracks, and ignites with even a static electricity spark. In order to contain a useful amount of hydrogen, bulky, expensive hydride tanks, expensive cooling machinery, or extremely high pressure apparatus are needed, all of which more than offset hydrogen's advantages.

Hydrogen fueled PEM technology currently leads the industry. It has many important advantages, but is not without multiple weaknesses. An in depth analysis of the challenges facing PEM technology can be found in appendix A.

A fuel cell electrode that can run directly on liquid fuel such as petroleum, methanol, or dissolved borohydrates would solve many of the industries problems. Methanol is a fairly ideal fuel. It is colorless, odorless, energy dense liquid. Unlike hydrogen, methanol is easy to manufacture, store and transport with the existing infrastructures. It is inexpensive and does not need to be cooled or pressurized. It is available ubiquitously and can be manufactured locally form agricultural waste. Methanol has the added benefits of being a sustainable and environmentally friendly fuel source. Methanol has virtually none of the storage dangers of hydrogen, and there already is an existing infrastructure that can distribute it.

Unfortunately, as yet, the direct methanol fuel cell technology has not achieved commercial viability. The current art has serious 'balance of plant', efficiency, cost, crossover, poison sensitivity, and longevity problems. They don't use the fuel efficiently and require greater amounts of precious metal catalysts. The electrode improvements described herein solve many of the hurdles facing direct methanol and many other types of fuel cells.

Objectives

I have invented a family of improvements and processes that allow for the manufacture of fuel cells that are less expensive, longer lasting, less sensitive to common poisons have greater power densities, and can run on especially liquid fuels such as methanol. The parts can be used to enhance other fuel cell designs, or collectively in a new and vastly improved fuel cell system. These designs lend themselves especially to direct methanol or borohydrate powered fuel cell applications, but can be utilized with a broad range of fuel stocks.

Specifically, the objectives of these designs are to provide improved fuel cell electrodes, components and processes that, compared to the current state of the art, are:

> <u>Much</u> less expensive to build.
> Longer lasting.
> Much more efficient, powerful, and can have a much higher energy density.
> Able to operate using on a variety of inexpensive and readily available fuels, including methanol.
> Able to eliminate the sensitivity to poisoning by carbon monoxide and sulfur compounds that currently severely limits the lifespan, feasibility, and commercial viability of the current art fuel cells.
> Able to use little or no platinum with the ability to employ multiple types of advantageous catalysts.
> Able to function with much less balance of plant apparatus.

- 3 -

> Able to utilize catalysts more efficiently, decreasing necessary catalyst loadings *especially to achieve or surpass the goals set forth by the US Department of Energy for fuel cell loading.*
> Able to incorporate a means of reducing or eliminating electrolyte degradation.
> Less sensitive to vibration and wear.
> Able to eliminate water balance issues.
> Part of a potentially rechargeable fuel cell.
> Capable of electric and/or magnetic field augmentation of mass transport and diffusion as well as advantageous charge bilayer manipulation.
> Ready for broad commercialization.

Advantages

This new electrode technology enables the creation of a new type of fuel cell that does not have the barriers to broad commercialization that hold back current art. These designs could more than halve the cost of fuel cells. The components can use multiple fuels, especially methanol and sodium tetrahydroborate. They last much longer than current art and are less sensitive to vibration and wear. They have smaller stacks with increased power densities and less balance of plant apparatus. They are less sensitive to ambient or operating conditions and are scalable to a broad range of applications. They should penetrate deeply into the largest range of fuel cell consumer markets.

Advantages Explained

Increased efficiency

These components and processes utilize catalysts and fuels more efficiently than the currently available designs.

- Utilize their catalysts much more efficiently with respect to available catalytic surface are to utilized mass.
- They have better substrate/catalyst interaction that greatly increases the reaction rate and current density.
- They enable faster mass transport.
- They eliminate concentration gradient efficiency losses.
- Ohmic losses are reduced by an order of magnitude. The internal resistance and impedance are nearly insignificant, certainly much lower than in any commercially available fuel cells.
- The flow through operation allows for more efficient water handling.
- There is substantially reduced fuel crossover.
- They employ a novel, simple, self-regulating, non-parasitic means of thermal and water management.
- The flow-through design allows oscillating flow.
- They do not rely on triple phase interaction for the reaction to take place.

Another means for efficiency gains embodied in these designs is the ability to use a means to manipulate and optimize the charge bilayer and ionic flow conditions.

Less catalyst requirements

They provide greater overall catalyst surface area <u>and</u> greater catalyst surface area to mass ratio, decreasing necessary catalyst loading. Further, the design intrinsically eliminates many of the causes of decreased substrate/catalyst interaction. Therefore less catalyst and/or less expensive types of catalysts can be used, decreasing costs. They achieve and surpass the goals set forth by the US Department of Energy for fuel cell catalyst loading.

Lowered materials and manufacturing costs

The new electrode designs lend themselves to ease of inexpensive mass manufacturing. Depending on the manufacturing processes employed, they can be made on one machine.

Current designs for low temperature fuel cells employ field flow plates. Up to 80% of the volume of the fuel cell stack and a large percentage of the cost is for the field flow plates. The designs described below do not require field flow plates, further decreasing costs.

The increased overall current density and novel means for eliminating field flow plates and diffusion layers improve the energy density of the stack. This allows the manufacture of smaller less costly but just as powerful fuel cells, which in turn increases the range of applications.

Decreased balance of plant

Taking greater advantage of intrinsic synergies, fuel cells with these electrodes can utilize much simpler water balance, thermal management, current collection, and electrolyte management systems. The cell will require up to 90% less physical balance of plant supporting apparatus, such as pumps, current collectors, heat exchangers, evaporators, belts, hoses, controllers, interconnects, wiring, etc...

Because the improved electrodes can be part of technology that enables fuel cell stacks to be built without the added cost and bulk of field flow plates and because less electrode volume can be used, the stacks themselves can be significantly smaller than comparable current art devices.

Ultimately, these savings in equipment decrease the cost of materials and manufacturing, while eliminating much of the current art's parasitic energy drains.

There will be less required maintenance and less parasitic efficiency losses from balance of plant apparatus. Again this will increase efficiency and decrease cost.

Greater durability and longevity

Compared with the current art, these electrodes have much better structural integrity and are less sensitive to vibration, wear, and corrosion. They employ a means of eliminating the build up of the toxins that degrade the catalysts and shorten the cell life. They will also be refurbishable and recyclable by the manufacturer.

A permutation of these designs incorporates or allows for a means of reversing the natural degradation of the electrolyte that occurs over time, which will extend cell life.

Because they allow for designs with reduced balance of plant systems there is less equipment to break down. Simpler is better. These features confer markedly increased durability and longevity.

Better fuel selection

Low temperature fuel cells tend to use hydrogen as a fuel. Hydrogen is volatile, explosive, and expensive. It makes metals brittle and escapes trough microscopic cracks. Storage techniques are too bulky, expensive and/or risky. Further, there is no adequate infrastructure for hydrogen storage and distribution.

These electrodes can run on a variety of fuels that do not have the above problems, including methanol, ethanol, and borates.

Reduced water balance issues

Current fuel cells are very susceptible to water balance problems. They need to have a specific degree of water concentration at each part. If any part gets too dry or too wet, it will malfunction. This problem is especially important because waste product water is formed at one electrode, which can flood it, and water is dragged from the other electrode drying it. Furthermore, fuel cells operate in changing ambient humidity and encounter frequent temperature fluctuations.

This creates a cell stack that is essentially never functioning optimally, is quite sensitive to ambient and operating conditions, and requires additional water handling equipment that parasitizes the efficiency.

The natural synergies of my new design crate a cell that is essentially impervious to the kinds of water balance problems that can paralyze the current art. They obviate the need for most water handling equipment.

Decreased sensitivity to contaminants

These electrodes can incorporate a means to refresh themselves while inside the fuel cell to prevent poisoning by sulfur, carbon monoxide and the like.
Further, they can be factory refurbished or recycled for a still longer usable life span.

Applicable to a greater range of markets

Because of the improvements to these anodes fuel cells can be built that:
- Cost much less and last much longer
- Operate on multiple fuels especially methanol and sodium tetrahydroborate
- Are less sensitive to ambient or operating conditions and poisons
- Operate at a wide variety of internal temperature and pressure conditions
- Are scalable to a broad range of applications
- Are available for multiple types of catalysts

Fuel cells using these designs should penetrate many mass markets.

Aspects of the invention and its parts should become evident with reference to the following drawings and descriptions. It should be understood that there are many permutations of the following disclosure that can be made without departing from the scope or spirit of the present invention and its derivative works. It should be further understood that these drawings are diagrammatic in nature. As such, they may not be to scale and may be symbolic of the underlying principal without exactly diagramming the structure.

Drawings

Figure A: Current design electrode and electrolyte assembly.

Figure 1:   Diagrammatic representation of a side elevation of the improved anode with magnified views.

Figure 1A: Rectangular flat plate porous flow through anode. The arrow represents flow of fuel/electrolyte mixture.

Figure 1B: Magnified cross-section view of a diagrammatic representation of the gross microstructure of the porous flow through anode of fig 1A.

Figure 1C: Magnified view of a diagrammatic representation of the fine microstructure of a porous substrate with catalytic coating of fig 1B.

Figure 1C(a): Alternate microstructure of sintered particles. May be coated with, or made of, the catalyst.

Figure 1C(b): Diagrammatic representation of a porous substrate with voids filled with catalyst supporting particulate surface area expanders. They may or may not be sintered in.

Figure 1C(c): Diagrammatic representation of a porous substrate with voids filled with high surface area particles such as flakes. They may or may not be sintered in.

Figure 1C(d): Diagrammatic representation of a porous substrate with voids filled with grown in nanostructures.

Figure 1C(e): Diagrammatic representation of a porous substrate with hollow walls and catalytic coating on just one side. The coating may be applied to both sides.

Figure 1C(f): Diagrammatic representation of a porous substrate made of catalytic/ conductive material.

Figure 1C(g): Diagrammatic representation of a porous substrate with nonconducting substrate with conductive/ catalytic coating.

Figure 1C(h): Diagrammatic representation of a porous substrate with attached high surface area particles.

Figure 2A: Side view diagrammatic representation of 2 sided anode with central less dense, larger pore, high flow core for fluid ingress.

Figure 2B: Side view diagrammatic representation of a side view of an anode with pore size gradient across the thickness for increased surface area without increased resistance to flow.

Figure 3A: Side view anode with closely applied relative fuel barrier membrane at the egress side.

Figure 3B: Side view anode with relative water barrier semipermeable membrane applied to the ingress side.

Figure 4a: Diagrammatic representation of a fuel cell design with fuel separating membrane in the pre-stack electrolyte circuit and a nonselective permeable membrane between the anode and cathode.

Figure 4b: Diagrammatic representation of the stack design of figure 4.

Figure 5:   The stack case showing one possible way of orienting the fluid and air intakes and outputs.

Figure 6:   Sketch of manifolds placement relative to the stack case.

Figure 7A: Side view rarified core anode surrounded by two cathodes.

Figure 7b: Side view of a flow through anode surrounded by two cathodes.

Figure 7c: Side view of a single cathode paired with a more massive anode.

Figure 8a: Diagram of separated anodes and cathodes permutation demonstrating differential number of anodes vs. cathodes and different flow speeds in each compartment.

Figure 8b: Diagram of separated anodes and cathodes permutation demonstrating differential anode and cathode morphology for optimal performance.

Figure 9:   The water, thermal, pressure management system.

Static Descriptions of Diagrams

Figure 1 the diagrammatic representation of the improved anode shows the anode in a flat plate configuration as seen from the side, with magnified views. Wavy arrows (4) represent the electrolyte and fuel mixtures flow through the porous body of the anode (2).

Figure 1B shows a magnified diagrammatic detail of a cross section view of the gross microstructure of the porous flow through anode. (6) represents thin walls separating microscopic flow through channels (8). The fluid electrolyte mixture (10) flows through the space (8) by the wall (6) via pore (15).

Figure 1C shows a still greater magnification of the structure in 1b detailing the composition of wall (6). In this particular example solid framework (12) is coated with a catalytic/conductive thin film (14) creating complex (15). The fluid flows over the thin film (14) through the channels (8).

Figure 1C(a) shows an alternate microstructure wherein micro particles (1) have been sintered to form the body of the porous anode. The particles may have high surface are morphology, the may be coated with a thin film catalyst. The coating may be discontinuous. For a greater catalyst dispersion and greater ease of sintering the particles can be coated in a patchy or splattered/scattered pattern rather than continuously and/or the catalyst coated particles can be mixed with uncoated particles. In alternate embodiment, catalyst particles are mixed with particles with less or no catalytic activity.

Figure 1C(b) shows an alternative embodiment in which a porous framework (30) has voids filled with particles (32). These particles may be analogous to the current carbon supported platinum matrix or they maybe analogous to Figure 1C(a)'s catalytic coated sintered particles.

Figure 1C(c) shows an alternate embodiment where a porous framework (a) represented diagrammatically by (30) has the voids filled with high surface area flakes or particles (34). These flakes or particles may be composed of catalytic materials or alternately have a core of a different substrate than the catalytic coating.

Figure 1C(d) shows an embodiment in which porous substrate (30) has had nanostructures (28) such as nanohorns or nanotubes grown into space (8).

Figure 1C(e) is an alternate embodiment in which the porous substrate has hollow walls (16) with catalytic coating (14). The catalytic coating (14) may be on all sides of (16) including the interior (not shown). (18) represents a pore to the interior of the walls. (20) represents the interior of the walls.

Picture 1C(f) is a diagrammatic representation of a porous solid core substrate wherein the material (22) directly provides catalytic and conductive function without coatings.

Figure 1C(g) porous substrate (26) is composed of an inert material with catalytic and conductive coating (24) porous substrate.

In figure 1C(h) high surface area particles (27) are on the porous substrate(29)

In figure 2A a diagrammatic representation of a cross sectional view of a flat plate anode is shown. The anode is comprised of outer layers (38) with a very high surface area, small channel diameter and a large number of pores per inch for maximizing surface area. This electrode embodies a central core (40) composed of similar material but with greater pore size diameter and relative lower density than in exterior (38) to allow for the influx of the fuel electrolyte mixture (36).

Figure 2A is a diagrammatic view of a cross section of a flat plate anode. In this case three distinct zones (42, 44, 46) are displayed. These layers demonstrate an anode design with the area facing the fluid ingress (42) being maximized for high flow low resistance conditions with large pores and less relative density. (44) is an intermediate zone with medium pores, medium surface area and medium resistance to flow. (46) is a high surface area, small channel relatively higher resistance to flow region maximized for surface area for catalytic surface area fluid interactions.

Figure 3A shows a cross section of electrode (48) with corresponding membrane (50). Membrane (50) is located in a downstream fashion from electrolyte (48) in the flow of the fuel\electrolyte mixture (47). Membrane (50) has the properties of being semi permeable. It acts to selectively impede the fuel (51) while allowing the water and electrolyte mixture (49) to pass.

In figure 3B electrode (48) has a membrane (52) that is positioned upstream of the fuel electrolyte mixture flow path (47). Membrane (52) has the property of selectively impeding the passage of water (49) while allowing the fuel (51) to transmigrate into anode (48).

Figure 4 is a diagram representing a fuel cell electrode complex with electrolyte/fuel flow circuit. Showing an alternate embodiment in which membrane (56) is positioned in chamber (58) outside of the fuel cell stack. Fuel, water and electrolyte mixture enter by port (60). Membrane (56) selectively impedes water while allowing fuel to pass through it. The relatively fuel depleted egress (61) travels through conduit (64) into space (72). The space between cathode (68) and anode (76) is divided by porous non-selective permeable barrier (71). In this representation the side of cathode (68) facing away from the fluid has hydrophobic membrane (66) that allows airflow to permeate into cathode (68). Cathode channel (72) is a closed space, which experiences the relatively continuous influx of fluid (61). This creates hydrostatic pressure that causes a net egress of the fluid in space (61) into the space (74) across membrane (71). The relatively concentrated fuel mixture (63) is transported to anode space (74) via tube (62). There it permeates and filters through anode (76) to where it is collected in space (78) and returned via conduit (80) to fuel processing box (58). (54) represents the system by which additional fuel is added into stream (63) via injector (55).

Figure 4b is a diagrammatic representation of the association of stack components described in 4b individually. (82) is the manifold by which high concentrate fuel mixture is brought into space (96). Manifold (84) brings low fuel high water flow into space (92) by cathode (90), which is covered, on the contra lateral side with hydrophobic porous membrane (88) that allows air (102) to permeate into cathode (90). The fluid in cathode space (92) filters via hydrostatic pressure across permeable separation membrane (94) into space (96). The 2 fluids mix and permeate through anode (98) into space (100) where they are transported back to the balance of plant apparatus by manifold (86).

In figure 5 ones sees a corner elevation of the exterior of the case for the fuel cell stack (104). (104) has openings (106) along one face for the ingress of air with similar openings on the opposite face (110) for air egress. Case (104) on sides perpendicular to (106) has slots (108) for the ingress of the fuel electrolyte fluid and similar spaces along the opposite face (112) for the egress of fluids. In this diagram the electrode plates would be holding the interior of the case in water/airtight channels. The electrodes would be flat thin plates oriented parallel to face (104) between the various slots (106,108). An alternate embodiment the entering liquid and/or air can egress on the same side to form a counter current multiplier to preserve heat within the stack (not shown).

In figure 6 the fuel cell stack case (104) is shown with one embodiment's relative positions of air and fluid manifolds. Fan (103) blows air into manifold (128). The air passes through the slots in case (104) between the hydrophobic layers of the cathodes. The air egresses through manifold (124) over coil (126). The fluid ingresses through tube (116) into manifold (114) through slots in case (104) through the porous anodes out

through slots on the contra lateral side of (104) into manifold (118) and out through tube (120).

Figures 7A through c show 3 alternate anode/cathode configurations/relationships.

In figure 7A anode (135) is comprised of high surface area external sections (138 and 142) with a relatively rarefied or even hollow area (140) is sandwiched between cathodes (136), which have hydrophobic membranes (132) on the contra lateral side. Depending on the direction of circulation, fluid enters or leaves through the space between the cathode (136) and anode (135). It filters through the porous walls of the anode (138 and 140) into or from the space (140). In this embodiment the fluid flow direction augments the mass transport of the hydroxyl species.

In figure 7b flow by anode (144) is sandwiched between cathode (136), which have hydrophobic membranes (132). Fluid flows into spaces (134) and by the anodes and cathodes.

In figure 7c relatively thicker anode (146) is paired with cathode (136). Fluid ingresses through anode (146) from the side contra lateral to cathode (136) and out through the space between anode (146) and cathode (136). It may flow in the opposite direction.

Figure 8a shows an alternate stack structure in which the anodes are grouped together in a chamber relatively separated from the cathodes. Injector (154) injects fuel into the fluid in space (152). This fluid is circulated into the anode room (153) where it flows into channels (156) through the anode (157) and into the spaces (158). The fluid then is collected into space (160). It is circulated into the cathode room (155) where it flows into channels (148) between cathodes (150). Air circulates between channels (151) on alternate sides of the cathodes from the fluid. Fluid then flows out into space (152). The significance of this diagram includes the fact that there are different number of anodes and cathodes. Flow channels (148) and (158) have differential flow characteristics including total cross sectional area and length designed to alter the fluid flow dynamics to maximize either anode or cathode function.

Figure 8b is a schematic diagram representing the flow circuit of alternate fuel cell stack embodiment wherein the anodes and the cathodes are grouped together relatively separated from one another. Pump (190) circulates fluid past (160), which injects additional fuel. The high fuel mixture flows through conduit (162) into the intra anode space (164). The anodes (168) are relatively short and thick compared to the cathodes (178). The fluid permeates and filters through anodes (168) into collecting systems (170 and 172). It flows by conduit (164) into the cathode chamber (175) and into the intra cathode space (176). Air flows through the contra lateral sides of the cathode from the fluid via channels (177). The fluid is collected in manifold (18) and returned to pump (190).

The details of these inventions set forth in this application are set forth in an illustrative manner. Those skilled in the art will recognize that these inventions may have additional embodiments or may be constructed without several of the details described herein.

Components and how they work.
Background: The current art anode inefficiencies:

With reference to figure 1A, in the most common forms of current art PEM and most direct methanol fuel cells, the anode is composed of a mixture is finely divided, widely dispersed very small particles of platinum dust supported on, and adhered to, larger, but still microscopic, carbon particles.

The substrate and catalyst complex is mixed with an adhesive binder to hold it together, fibers to increase structural integrity, and hydrophobic PTFE to help the egress of water. This mixture is applied to a structural support (in PEMs the support is often the electrolyte membrane itself). Applied on the contralateral surface is an electrically conductive felt like gas diffusion layer then the field flow plate.

This current design is functional and an improvement over earlier designs, but it is still vastly inefficient. Especially in the case of direct methanol fuel cells, this form of electrode suffers from several problems:

- Only a small fraction of the mass of the catalyst is available for catalytic activity.

  The catalyst molecules on the surface of the catalyst particle are the only part that touches the fuel. The rest of the mass of the catalyst is trapped in the interior of the particle where it cannot touch the reactants. We can calculate how much of the expensive catalyst is wasted in the above manner with some simple equations. Assuming the particles are roughly spherical: The formula for the volume of a sphere is:
  $$V= 4/3(pi)r3$$

  The formula for the surface area of a sphere is:
  $$SA=4(pi)r2$$

  So, the ratio of surface area to volume of a sphere is:
  $$S/V=3/r$$

  Standard catalyst particle radii for PEM cells are 12.5-24.5 angstroms. Therefore, in PEM cells, the ratio of surface area to volume ranges from 1:4 to 1:8, with 1:6 as a median. Only about 1/6th or 17% of the platinum is available as a catalyst at a time, roughly 83% of the mass is wasted. The waste is much worse in direct methanol fuel cells. They require larger particles and heavier loadings. Direct Methanol cells generally employ particles with radii of roughly 44-125 angstroms. Plugging these numbers into the above equations reveals that the surface area to volume ratios vary from 1:15 to 1:41 with a median of 1:28! Therefore, only 3.6% of the

catalyst is available surface area. The rest is potentially wasted by being locked inside the particle.

Further, part of the 3.6-17% of platinum that is the surface is additionally lost to the reaction because it is in intimate contact with inert substrate materials such as PTFE, glues, structural fibers, or the carbon support itself. This contact area excludes contact with the reactants. This further limits the usable, catalytic surface area. Losses from these contact areas can be conservatively estimated at about an additional 5%.

Additionally, another loss of catalytic utilization occurs because the reaction can only take place at the triple-phase interface of the fuel, electrolyte, and catalyst. Only a fraction of the catalytic mass, left after the above reductions, encounters the triple phase electrolyte/fuel interface. Even in the case of the particles that do touch the interface of fuel and electrolyte, not all of the surface area experiences the interface. A significant amount of the catalyst does not even touch the both phases and electrolyte simultaneously, and therefore does not participate in making electricity. Further, those particles that do experience a favorable interface produce or use water, thereby changing the fuel and water ratio in their immediate microenvironment, often decreasing catalytic efficiency.

The bottom line is that even with the recent advances, the current art suffers from tremendously inefficient catalyst utilization, in the range of orders of magnitude.

- The materials and mixture of the current art are fairly electrically resistant. The adhesive binder is PTFE, which is highly nonconductive. The electricity has to flow through multiple interfaces of the carbon particles and PTFE coatings then through the diffusion barrier and then through the field flow plate. Each of these compound, especially the PTFE contributes to the overall internal stack resistance and the interfaces of each material junction (i.e. platinum to PTFE to carbon particle to PTFE to carbon particle.... to diffusion layer to field flow plat to busbar). Contributes to impedance losses. These internal losses substantially decreases electrical production efficiency and necessitates the use of conductive current collecting field flow plates that add sizeable cost and volume to the stack.

- The carbon platinum mixture is a brittle composition of dust; a composite of powders. It is sensitive to vibration and mechanical, electrical and thermal stresses. Over time it tends to disintegrate limiting lifespan and efficiency.

- The fuel flows by or into the electrode, but not though it, so inert compounds can build up in the pores and physically block the fuel from reaching the catalyst further limiting efficiency.

- The individual parts of the fuel cell stack need a uniform, fairly exact degree of humidification in order to function. Because water is made at one electrode potentially flooding it, used up at the other drying it, and dragged by concentration gradients and electro-osmotic forces, extensive, costly and power robbing balance of plant apparatus has to be added. Even so, the simultaneous ideal humidification for each part is never quite uniformly achieved.

Each of these efficiency losses either directly or indirectly affects a tremendous drop in the actual electrical production efficiency and utilization efficiency of the catalyst, electrode, stack and overall system.

What is being patented: <u>The improved electrode design specifics</u>

The basic concept is an electrode for fuel cells with a continuous, flow through, open celled, porous, electrically conductive structure with a thin film catalytic coating and a means of refreshing the catalyst against common poisons. As described below the substance and shape of the electrode can have many variations. What is important is that fuel and/or electrolyte fluid flows through the porous body of the anode, over a tremendous, and refreshable, thin film catalytic surface area. Rather than the industry standard of highly dispersed catalytic particles scattered within a relatively poorly conductive substrate, the catalyst is a thin film coating that may or may not be contiguous, on a substantially electrically conductive, flow trough porous media.

The advantages of the flow through design, synergistically with the advantages of using thin film catalytic coating, confer several greater advantages than the sum of these two processes operating separately. The flow through design, paired a thin film catalytic coating, confers many additional new advantages over the current state of the art designs. The electrode is designed to have good internal electrical conduction for integral current collection. It may have that ability intrinsically from the properties of is constituents, or additional means of achieving this superior conductivity may be applied. The fuel mixture flows through the electrode, rather than just by or into it. In a preferred embodiment, the catalyst is a thin film coating on the extensive surface area throughout the sintered or foam metal, or on a porous conductive polymer porous electrode. (See Figure 1).

Theses designs are different from the next closest technology in several important and advantageous ways. The catalyst, being a thin film, presents a much higher active surface area per mass of catalyst material ratio than any other methods and therefore achieves one of the several ways they increase the catalyst utilization efficiency. That surface area is intimately applied to the porous substrate creating a substantially better electrical and physical connection, creating a sizeable reduction in the impedance and internal resistance losses suffered by the current designs. The surface area is laid out in such a way that it is cleansed of efficiency sapping concentration gradients by the flow through and detergent characteristics of the electrolyte. This, also, is one of several advantages not available to the incumbent technology's dispersed particulate catalysts.

The electrolyte and fuel are presented in a novel fashion so as to interact much more efficiently than in the current art, boosting overall efficiency significantly. There is no need of the triple phase interaction and its inefficiencies.

This novel design also enables the means of electrically cleaning the catalyst described below. Were such a process used in the current art, the gasses would cause the carbon components to disintegrate. The gasses would dislodge the catalytic particles, and break down the slightly porous field flow plates and electrodes. It would also be formed and disadvantageous areas.

The advantages of the flow through design, synergistically with the advantages of using thin film catalytic coating, confer several greater advantages than the sum of these

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two processes operating separately. This also allows the electrodes to function without the expense, bulk and efficiency losses of the current art's field flow plates, diffusion layers, current collectors, and water balance issues.

This technology is especially suited to liquid fueled fuel cells, but can be used with PEM, gas fueled, and other types of fuel cells.

Electrode Design

A variety of configurations and manufacturing processes can provide the needed characteristics for a conductive, flow through, high surface area, and refreshable design. Some permutations of the base microstructure configuration include, but are not limited to: open cellular, reticular, foamed, sintered, conductively adhered particles, sponge, raney, nanostructure, vitreous, molecularly bonded metals, aero-gel type substructures, etc.

The microstructure of the material is engineered with respect to porosity, pore size and shape, wall size, shape and thickness, as well as density to maximize surface area of available catalyst/substrate interaction, while preserving desired flow-through characteristics. Each of these parameters will be tuned to the specific requirements of the individual application. An ideal configuration from a structural standpoint is an open cellular thin walled sponge with a thin film coating. An ideal configuration from a materials cost, forming and manufacture standpoint would be an adhesed or sintered conglomerate of partially or fully coated particles. The important factor is that the pore volume, and shape be optimized for both flow and maximal catalyst surface area. The walls may be hollow (figure 1C(e)).

Materials for the substrate include porous conductive plastics, carbon compounds including but not limited to graphite, carbon, aerogels, and carbon black, ceramics, and metals. Stainless steel and nickel are to some extent preferred, but a variety of materials, mixtures and alloys are considered viable and even advantageous under specific conditions. These materials include, but are not limited to nickel, silver, molybdenum, titanium, ceramics, and carbon composites. There are several porous carbon structure with useable characteristics.

One of the more promising possible electrode bulk structure manufacturing processes uses a specific form of sintering. In this process, a base material's particles are coated with a thin, possibly discontinuous, layer of catalyst. The catalyst coated base particles are then sintered into an extremely high specific surface area, flow through, coated porous electrode. A mesh of fine wire may be incorporated to promote conduction. This method bypasses the pore size limitations of electroless plating and creates very high surface area to volume ratios, but has the added challenges of maintaining the uniformity of the coating layer during the sintering process. Higher pressure, lower temperature techniques enable this method. There is considerable advantage from using odd shaped, high surface area particles such as twisted flakes, filaments or a combination of shaped particles.

A similar embodiment involves the use of a porous reticular metal substrate. Depending on the method of manufacturing employed to make the structure porous, additional means may or may not be employed to increase the available surface area. One such means includes sintering, adhering or growing additional substrate(s) into the voids of the porous material (figure 1C(b)). This is often necessary to achieve the needed

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surface area. This sintered material may be coated metal particles (figure 1C(c)). Traditional carbon supported catalyst can be retained in the voids also.

In general, the goal is to produce an electrode that is less than 3mm thick and embodies 5-10 or more square meters of catalytic surface area exposed to the fuel/electrolyte mixture per cm2 of the electrode's flat face. Average pore size goals are in the vicinity of .01mm, but there is a considerable range of possible sizes. Wall configuration is optimized for maximal thinness, preserving structural integrity and conductive function. Depending on design and application specifics, there is considerable variation of practical densities, porosities, pore sizes, etc.

Current embodiments have also utilized a nickel or nickel chromium base reticulated foam substrate with various pore sizes. The available surface area is variable but includes 5600cm2 SA per cm@ outer surface. Various methods for augmenting the surface area described herein are utilized to boost the available surface area. This brings the surface area to the range of some of the current art's calculated theoretic particle surface area. However, because the catalyst is used so much more effectively, much less catalyst may be used while achieving much greater efficiency.

The electrode may be directly composed of the conductive catalyst/ catalytic mixture (figure 1C(f)) or may embody a different base material with a thin film coating(s) for conductive and catalytic function (figure 1C(g)). The catalytic layer may be mixed with or layered on substances to increase conductive function. The porous substrate is either electrically conductive itself or it has conductive additives or coatings. It acts as a low resistance integral current collector.

Edge connection utilizes less material and simple off the shelf busbar design. It is the least expensive form of collecting system to manufacture. The walls may include a dielectric layer between two conductive layers to create a capacitor effect. The core may be a polymer/ceramic combined with a metallic conductor and/or catalyst.

Materials can be selected and blended/alloyed/ combined for conductivity (silver, molybdenum, etc), catalytic activity (platinum, palladium, ruthenium, manganese, silver, etc), cost (nickel, etc), or corrosion resistance (stainless steel, etc).

The catalytic coating may have several different compounds therein mixed, alloyed, layered etc. An example would be a layer of ruthenium with an overlying or intermixed platinum and/or palladium and/or molybdenum component. Certain additives may be included to help weaken the carbon monoxide or sulfur group poison interaction with the catalyst.

The surface of the base porous structure may be pre treated with various oxidizing means or other pre treatments to enhance the deposition of the catalyst. There are many possible deposition methods available including PVD, EVD, CVD, chemabsoption, electroless, etc.

The electrode may embody a porous substrate combined with pasted, grown, or packed material in the voids for the enhancement of the surface area. An example of this would be a metal sponge in which the voids contain the current art's carbon supported catalyst mixture with the catalyst as a thin film instead of a particulate and the binder a more conductive material than PTFE. In another example, nanostructures such as nanotubes on nanohorns are grown or packed onto the porous base metal into the voids, or are used, directly, without the sponge substrate, for the dispersion of catalyst over a greater surface area (analogous to intestinal microvili) (figure 1C(d)). The catalyst can

coated on or be integral to the nanostructures. In another example, a powder of high surface area low mass flakes and/or particles are pasted, sintered, etc directly into the voids or as the base structure itself (figure 1C(c)).

The overall electrode can be manufactured in a variety of application-specific shapes and sizes. Categories of shape include, but are not limited to, flat plate, corrugated, tubular, conical, and cylindrical. The electrode may embody an area with less resistance to flow, surrounded by material optimized for surface area with more reduced flow-through characteristics (figure 2A). This is one means of optimizing substrate/catalyst interaction while reducing the potential to form activity-depleted regions within the body of the electrode. \

Another such permutation involves manufacturing a pore size gradient into the electrode (figure 2B). The larger pores are on the fluid ingress side with the fluid flowing into progressively narrower channels. This design increases the available catalytic surface area while not significantly increasing resistance to flow and helps eliminate fuel-depleted regions in the thicker electrode designs. A preferred permutation of this would be to have the higher surface area side experience the fluid ingress. This way the highest fuel concentration is applied to the greatest catalytic surface area.

With repsect to minimizing crossover losses, a variety of mechanisms may be employed, individually or in concert. The electrode may be engineered to embody hyrdrophobic or hydrophilic qualities that help preferentially to reltively attract either fuel or water molecules to that surfaces microenvironemt. The electrode may include, be applied to, or function in conjunction with a membrane that relatively separates the fuel from the fuel/water/electrolyte mixture. There are several permutations of this design concept. If a membrane that selectively retards the passage of fuel is employed, it can be positioned on the fluid egress side of the anode (figure 3A). This will cause a relative increase in the fuel concentration of the mixture within the anode, increasing efficiency. This would also cause the fluid reaching the cathode to be further fuel-depleted thereby decreasing the potential for fuel crossover losses. The membrane, in this location, needs to allow the passage of hydroxyl ions. A membrane that allows the passage of fuel but relatively blocks water can be placed on the fluid ingress side of the anode to increase the fuel concentration within the body of the anode for the same effect (figure 3B).

There may be additional catalysts specific to a separate, electrolyte replenishing reaction mixed in with, or in close association, with the electrode (described in a separate applicaton.)

Another embodiment employs the use of modified zeolytes as the anode body. These have ideal porosity surface area to volume ratios; they will need strategic modification to increase conductivity and to incorporate catalytic function. These methods include, but are not limited to, plating, deposition and mostly substitution of conductive and catalytic compounds. Zeolytes may be formed in the voids of a porous substrate.

Electrical conductivity of the electrode may be enhanced by several means. Highly conductive compounds may be used as a part of, or as a separate layer from, the base substrate and of thin film catalytic layers. The porous structure may have included in it fiber, filaments, or wires to enhance conductivity. It may embody areas of thicker substrate arranged advantageously for internal conductivity. One example of such can be visualized by picturing a large pore, macro-porous structure in which the voids contain a

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less conductive but higher surface area more micro porous structural permutation. Another example would be a conductive foam in which thin generally contiguous areas are filled in or composed of a better conducting material or permutation of the same material. In the example of the porous structure being similar to the current art's adhered carbon, a much more electrically conductive adhesive would be used than the PTFE binder usually embodied. This permutation also differs from the current art in that the catalyst is a thin film rather than dispersed particles.

A further permutation is the addition of a means to develop and control an electric and/or magnetic field that can increase mass transport, induce advantageous change in the electrode charge bilayer-.capacitor type. There may be an externally, or internally, applied means of creating an electric and/or magnetic field to elements of the stack such as electrically charged or magnetic compounds in or near the electrode. Such means include:

> A mechanism for inducing a cyclical fluctuation in the electricity exiting the stack. This could be as simple as a single rapid on/off chip in the electrical circuit. The off cycle would allow an increase in the local electric field potential, the on cycle would better allow the hydroxyl ingress. The ratio of time in each cycle can be set to optimize performance.

Similarly, a small charge can be introduced in either, or oscillating in both polarities to the circuit.

> An electric or magnetic field could be induced within the anode/ cathode space to hasten the mass transport of ions.

> A capacitor could be built into the body of the electrode for both of these functions, or it could be located adjacent to the electrodes. A permutation allows for an intermediate dielectric layer within the layered porous substrate for the creation of a capacitor field.

In PEM designs the porous electrode can be applied directly to the membrane. One embodiment has the electrode material laid out in strips. The flow is then directed generally parallel to the membrane through the short sides of the strip. Membrane substance can be mixed into the anode, preferably with a concentration gradient peaking at the membrane interface to increase proton conductivity.

How the electrode achieves its results:
      Efficiency Gains
      <u>Increased catalyst utilization efficiency- More available surface area per gram of catalyst</u>
      The catalyst, rather than being bound up inside particles and clogged with binders, etc, is a thin film coating on the extensive surface areas of the porous anode's channels (figure 1C(a)). A much higher percentage of the catalyst can be presented as usable surface area, as compared to the current art. The fuel flowing through the microscopic pores in the electrode is presented with much more catalytically active surface area per gram of catalyst than is possible with current designs. Therefore much less catalyst is needed. In fact, because the catalyst is used with such higher efficiency, other catalysts besides platinum can be blended into the coating further decreasing platinum loading requirements.

Increased catalyst efficiency- Increased reactant/catalyst interaction

In all fuel cells, in order for the reaction to proceed, there needs to be a triple interface of catalyst, fuel and electrolyte. The reaction only occurs at the interface of all three compounds. If one of these components is not in direct contact with both of the others at the same time, that area will not contribute to the reaction. In the prior art, even under theoretical, (unachievable) ideal conditions, a very significant portion of the catalyst particles do not experience the triple interaction and are therefore wasted. They simply do not touch both the fuel and the electrolyte, as is required for the reaction (See figure A.)

These new designs apply the three components of the triple interface together universally. The fuel is dissolved into the electrolyte, so both are in continual and complete interface. Functionally, every molecule of fuel touches a molecule of electrolyte. The fuel/ electrolyte mixture then flows, through the porous electrode, over a tremendous surface area of active catalyst. The reactants are applied to the catalysts with orders of magnitude greater efficiency than in the incumbent technology they will replace. The area of triple interface is many times larger than in the prior art. Unlike the current art, 100% of the surface area is utilized 100% of the time. Simply put, unlike in the current art, much more of the catalyst, on a gram per gram basis, is actually used for making electricity. So, not only do these designs embody a much greater amount of useful catalytic surface area, essentially every molecule of that catalytic surface area experiences the triple interaction and contributes to the reaction. This is true even though less catalyst is used than in the current designs.

The increased catalyst surface area boosts the reaction rate, current density, and efficiency of the electrode. Therefore, it is possible for this design to use less catalyst to get more power, achieving and surpassing the goals set forth by the US Department of Energy for fuel cell catalyst loading.

Decreased concentration gradient losses

In the current designs, as the substrate is used and product water is made at the electrode, a relatively substrate depleted microenvironment forms around the catalyst. This decreases efficiency by limiting catalyst/substrate interaction. This is worsened because relatively dead-end recesses paired with the lack of flow through design of the current art, trap inert compounds and waste products. These substances can build up, keeping fuel from the catalyst. The 80% of air that is not oxygen, inert products in the fuel stream, and even the product water formed on the catalyst can get trapped and block fuel or ions from reaching the catalyst. Collectively this microclimate scale "gumming up" of the catalyst is termed 'concentration gradient loss.'

The flow-through design, surfactant nature of the electrolyte mixture, and oscillating fluid flow of the new designs all serve to break up concentration gradients before they can form, preserving maximal reaction rates.

Fluid flow is net forward but oscillates back and forth. This not only helps mix the fluids, it forces additional substrate to interact with the catalyst each pass. The net effect is that the substrate encounters much more catalyst area as it passes though the electrode, increasing efficiency again.

Reduced ohmic losses

More efficiency gains over the current art are gained in the area of electrical conduction. The current art, with its poorly conducting carbon and nonconducting PTFE components, suffers from a very high internal resistance. Simply, the base materials are relatively poor electrical conductors. This saps a significant percentage of the available voltage, wasting efficiency. To partially atone for this, designers of the present technology have had to include field flow plates that are also current collectors, adding cost and complexity while seriously dropping the power density.

Reduced ohmic losses are achieved by a number of means. First, in these new designs, the base materials and/or coatings are excellent conductors. Second, my design does not use binders on a discontinuous substrate, significant sources of electrical resistance in the current art. The internal resistance of my electrodes is essentially negligible. So much so that separate current collectors or field flow plates are not needed. They intrinsically have so little internal resistance that they can be edge connected. Incorporating various compounds directly onto or into the structure can further increase conductivity.

My designs also have much less electrical impedance. Impedance is the efficiency loss that occurs when electricity has to travel between the interfaces of materials with different conductivities. Impedance is minimal in my designs because the charge travels through only similar, intimately connected materials with very large interfaces. It can be further reduced, if desired, by including a small amount of the counter-interfacial compound to each layer. Additionally, my design has far fewer electrical junctures further decreasing impedance.

The dramatic increase in utilization efficiency and lowered catalyst requirements allow for the manufacture of fuel cells that achieve and surpass the goals set forth by the US Department of Energy for fuel cell catalyst loading.

Relative imperviousness to water balance issues

Current fuel cells are very susceptible to water balance problems. They need to maintain a very specific degree of humidification at each part. If any part gets too dry or too wet, it will malfunction. This problem is exacerbated because fuel cells operate in changing ambient humidity and encounter frequent temperature fluctuations. Furthermore, water is formed at one electrode, which can flood it, and water is used by, and dragged from the other electrode, drying it. The membrane is subject to both problems. This creates a cell that seldom functions optimally, is quite sensitive to ambient and operating conditions, and requires additional, bulky and prohibitively expensive, water handling balance of plant equipment. The water handling equipment electrically parasitizes the fuel cell, dropping efficiency.

Fuel cells with my new design are not affected by the kinds of water balance problems that plague the current designs. The product water is washed away as it is made by the flow-through design. Because the water makes up a large percentage of the electrolyte, these designs are impervious to the degree of changes of water concentration that would paralyze the current art. Excess water is removed by transpiration and/or evaporation elsewhere in the system with a self-regulating system that does not draw power. There is no need for the power drain of parasitic water balancing equipment

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required by the current art. The natural synergies of this design obviate the need for most water handling equipment, further substantially decreasing equipment requirements and cost while boosting efficiency.

Crossover dangers and efficiency losses

A problem with most fuel cell designs is that some of the fuel can get by the anode unused and wasted. This is called crossover and is deleterious in two fashions. First, the unused fuel represents wasted efficiency and increased pollution. Besides being wasted by not getting used, some of the crossover fuel can oxidize at the cathode further dropping efficiency.

These designs reduce fuel crossover efficiency losses by any of a series of features. In the first feature, the electrode is engineered with the specific hydrophobicity or hydrophilicity to attract or repel water or fuel as is advantageous to that specific microclimate's process.

A different feature in embodiments with anode to cathode flow direction, a large percentage of the fuel is used in the anode in a 'first pass effect.' Fuel utilization is augmented by specific flow rates and the oscillating flow. The fuel mixture is brought back and forth across the anode, utilizing a greater percentage of the available fuel, increasing the first pass efficiency. The little fuel that does make it through the anode becomes substantially diluted by the product water made at the anode. In the case of methanol, for every molecule used, 5 water molecules are made. Any fuel that makes it through the anode becomes diluted tremendously. For these two reasons, the cathode only experiences a relatively fuel depleted environment. Additionally, the cathode has catalysts with selectivity against the anode reaction, reducing crossover efficiency loss. The cathode also may include a number of fuel excluding technologies described in a separate application.

The second crossover problem is dangerous mixing. When crossover occurs, the current fuel cells can mix explosive fuel with oxygen in an electrically charged and heated environment. This dangerous condition plagues all low temperature fuel cells.

PEM design uses a tremendous area of membrane to separate the hydrogen from the oxygen. The membranes are paper thin and semipermeable. The gasses are hot, pressurized, and create caustic, reactive intermediary compounds that permeate the apparatus. Over time, the membranes develop leaks that allow mixing of hot pressurized hydrogen and oxygen inside a hot, electrically active device. It is a potential recipe for an explosion. Even if all other cost and efficiency problems were solved, there is still this dangerous problem with which to contend.

Fuel crossover mixing only occurs in an almost imperceptible degree in my design. The slight extent that it can happen is not unsafe, deleterious, or even significant. Such a small amount of methanol evaporates from the cathode that the fuel is diluted into literally millions of times more air volume so that there is no combustion risk. Further, my designs employ multiple means of reducing the amount of fuel that gets to and into the cathode.

In a embodiment described below, before the fuel mixture enters the fuel cell stack, it goes though a series of separators that serve to channel concentrated methanol to the anode, away from the cathode (Figure 4.) The fuel injectors also feed into only the

anode stream. The product water further dilutes any fuel left in the cathode stream. The cathode experiences a fuel-depleted environment, so very little of the fuel is available for crossover. The potential for fuel crossover is still further limited by the fuel-phobic nature of the materials within the body of the cathode. Very little fuel reaches the cathode, even less penetrates it, and the little that gets through is immediately washed away by such a hugely greater volume of air that it stays orders of magnitude more diluted than its combustible concentration.

Moreover, because the fuel is in liquid form, it does not mix in the same hazardous way that gasses do.

Decreased mass transport losses
In the current art, a significant bottleneck for the electricity producing reaction is the time it takes for the ions to cross the electrolyte. This is termed 'mass transit losses.' These new designs enable and employ a variety of ways of reducing this cause of efficiency loss. Oscillating flow mixes the electrolyte promoting faster ionic diffusion.

As described in another application, the buffers and dibasic compounds can release extra ions as needed at the appropriate electrode should the local microclimate become depleted. Also, the electrolyte replenishing means keeps the ionic concentration optimal. These electrodes allow for the use of a means for inducing an electric field across the electrolyte to hasten transport (below.)

Electric field modifications
Within the anode, a negative charge builds up. Because like charges repel, this negative charge concentrates at the surface of the electrode. The surface charge concentration creates an electric field that attracts positively charged elements to surround the metal. In my fuel cell, this charge bilayer serves to augment fuel catalyst interaction by attracting negatively charged intermediary compounds to the catalyst. It can also be disadvantageous in that it can repel the needed hydroxyl ions.

These fuel cell designs enable the incorporation of a variety of means for manipulating the charge bilayer to favor increased fuel molecular /catalyst interaction and/or increased ionic diffusion rates.

In systems where additional efficiency gains are desired, the electrolyte in the anode-cathode space can be subjected to an electric/ magnetic field. A capacitor can be situated next to, or within, the electrodes to hasten the diffusion of the negatively charged hydroxyls toward the anode (improving an otherwise rate limiting step) and limit the fuel and intermediary compounds interaction with the cathode. The capacitor also can provide the electricity for the refresh cycle and help smooth out natural current fluctuations.

Other features that are being patented
The refresh cycle
Background
Catalysts suffer from poisoning by common contaminants found in many fuel stocks. They are also poisoned by even their own reaction intermediary compounds. Poisons include a variety of sulfur and carbon based compounds. Of special importance

is carbon monoxide as it is a common intermediary compound of carbon-based fuels such as methanol. Overtime, these substances adhere to the catalytic particles of the current art electrode, degrading their performance and limiting the lifespan. Sensitivity to poisoning seriously limits the feasibility, lifespan, and commercial viability of the current art. It is especially a problem in fuel cells that use currently available fossil fuels and natural gas derivatives. They have relatively high amounts of sulfur compounds and complex hydrocarbons that form a variety of toxic intermediary compounds. To partially atone for this problem, manufactures are forced to incorporate expensive, additional balance of plant apparatus such as fuel stock scrubbers, reformers, shift reactors, and advanced filters. These are bulky and expensive.

They escalate cost, inefficiency, maintenance requirements, and pollution. The extra machinery also requires energy to run that is parasitically drawn from the fuel cell's output. The expense of the additional equipment obviates the advantages of being able to use readily available fuel stocks from the current infrastructure.

In addition to incorporating compounds into my electrolyte and catalytic coating to help solve this problem, my fuel cell design is uniquely suited to incorporate a refresh cycle that cleans the catalysts of poisons. In the refresh cycle, a specific electric charge is forced back through the electrode. At the catalyst, a specific amount of oxygen and/or hydrogen is formed, depending on the polarity of the charge. Especially the oxygen physically and chemically frees the catalyst of adherent toxins refreshing its function. The gas then dissolves, reacts with the catalyst to make water, or bubbles into the electrolyte and is cleared in the transpiration or venting equipment. It can also be used by the fuel cell.

The hydrogen can be caused to from at a specific, separate, electrode incorporated for the refresh function for appropriate handling. Studies are currently underway to evaluate hydrogen as a cleaning agent also. The electricity may be fed to the electrode with positive, negative, or alternating polarity for maximal cleaning/refreshing power with minimal gas production.

In the currently preferred embodiment, just enough gas is evolved to totally coat the catalyst in minute bubbles. The bubbles are small enough that buoyancy does not overcome the surface tension holding them to the catalyst. At the end of the refresh cycle, the small quantity of gas may dissolve, bubble off, or be reabsorbed at the electrode utilizing the fuel cell's own oxidation-reduction reaction.

In another permutation, enough gas is evolved to purposely cause bubbling of the gas off the electrode.

An interesting permutation utilizes the fuel cell's electrodes to create the hydrogen and oxygen in a new form of internal reforming. Using specific borohydrate fuel, hydrogen is made at the anode and oxygen is made at the cathode. Electricity is used to crack the hydrogen and oxygen out of the fuel stock. Then the hydrogen is consumed to produce water and heat. The net energy output is derived from the difference in enthalpies from cracking the fuel versus that for the hydrogen to water reaction.

This refresh cycle is especially advantageous in systems such as those with regenerative breaking, which periodically make bursts of electricity.

There is added advantage when the refresh cycle is incorporated into the operation cycle. That is, there are extra electrodes in the stack that are rotated through an

off/refresh cycle. For example, the stack calls for 100 MEA equivalents but incorporates extra units. Some of the extra units produce the power to clean and refresh a separate unit. A microprocessor rotates the roles of the electrodes as the fuel cell operates. This allows the refresh cycle to occur at higher temperatures and prevents build up, ensuring the greatest operation efficiency, while decreasing down-cycle maintenance time.

An alternate method is to have the refresh cycle occur as part of the start up and/or shut down procedure or as part of scheduled off cycle maintenance.

The cell can be caused to run hotter for refresh cycles by limiting the cooling flow or amount of cooling coils in the flow circuit.

Unlike the current art, this stack design is also amenable to periodically being flushed with specific gasses and/or liquids cleaners to refresh the catalysts.

Stack design

The fuel cell stack is housed in an inexpensive molded plastic box-like case. Construction and materials are quite similar to those for the casing of lead acid batteries. The anodes and cathodes are edge sealed into channels in the interior walls of the case. The case has slots on opposite faces for the ingress and egress of liquid and air. In the currently preferred embodiment, the air ingress and egress slots are on opposite sides of the case, perpendicular to the liquid's slots. (Figure 5) Simple manifolds carry the substrate fluids to and from the appropriate slots. (Figure 6) The manifolds are segmented to provide long thin channels that prevent internal electrical currents. In an alternate design, liquid ingress occurs next to egress to provide an intrinsic countercurrent heat exchanger.

In current low temperature designs, there are equal numbers of anodes and cathodes. A source of current art fuel cell efficiency loss is anode vs. cathode kinetic mismatch. In many systems, the anode could function at a much higher rate, but the slower cathode limits it. In several instances, the differential in electrode kinetics is two orders of magnitude. Designers adjust for this by differential catalyst loadings on each electrode.

In the current art, the electrodes are grouped in functional units of single anode/cathode pairs. The functional pairs may be arranged in two fashions. They may be placed so that the anodes and cathodes alternate in an every-other pattern, with like electrodes facing one another across the field flow plate.

In my design, the electrodes can be arranged in novel, ways for additional benefit. Differential kinetics can be partially or whole balanced, not just within the range achieved by varying the loadings, but also by the use of additional cathodes or more massive cathodes (picture 7A-c.) The anode may be surrounded by greater cathode area that balances the reaction kinetics. In one permutation the anodes and cathodes are relatively separated. (Picture 8.) In this permutation, the disadvantage of vastly greater ion transport distance is surmounted by a variety of considerations:

> Increased flow rates
> Eliminated electrical crossover
> Decreased fuel crossover
> Increased fuel utilization at the anode

> ➤ Ability to maximize each type of electrode's performance without the need to account for the other.

The anodes and flow can be shaped for maximal efficiency without having to mach the anodes size or shape and vice-versa.

In the illustrated examples (figure 8a+b), the flow chamber for the cathodes has a greater cross-sectional volume than that for the anodes. This slows the fluid flow down to compensate for slower reaction rates at the cathodes, balancing the system. Because the hydroxyls are delivered by flow rather than by diffusion, the anodes can be designed thicker, allowing for wider pores to decrease resistance to flow and increased total surface area for greater fuel utilization. A side circuit can be added to recirculate unused fuel leaving the anode.

Electrolyte circulation route

For added benefit, my design can embody an electrolyte flow path that hastens the mass transport of hydroxyls speeding the overall reaction. Unlike the prior art, my fuel cell can have net current flow within the stack travel generally from the cathode to the anode. This helps cool the anode and, more importantly, speeds the rate at which the ionic transport occurs.

One permutation of the flow design is to modify the pump to create an oscillating flow. The fluid flows back and forth in small amplitudes, but generally forward. This has many advantages. It further breaks up concentration gradients, mixes fuel, cleans out precipitants, and hastens mixing. Fuel flowing through the anode is dragged back and forth over the catalyst, increasing utilization. Mass transport is hastened by three means with this flow pattern. The net flow washes the ions in the advantageous direction, the mixing agitation increases diffusion rates, and the backward flow temporarily increases the concentration of ions, increasing diffusion pressure. The oscillating flow and flow-through function not only increase fuel/catalyst interaction for better fuel utilization, they wash away the product water, and increase the rate of ionic diffusion. They also can reduce precipitate build up.

In another embodiment, the fluid circulates in an anode to cathode direction. The anode uses the fuel and adds water to the mixture, so the cathode experiences only a diluted, fuel-depleted environment that is highest in the water that it needs. This promotes cathode efficiency while decreasing fuel crossover losses.

In another embodiment (figure 4), the fuel /electrolyte/ water mixture passes through a separating chamber. Here, it is separated into a fuel rich (A) stream and a water rich (B) stream. The A and B streams may pass into the anode-cathode space on either side of a porous flow limiting permeable barrier. This barrier is just obstructive enough to limit the A stream from appreciatively mixing back into the B stream. The B stream comes in on the cathode side of the permeable membrane, supplying a low fuel, high water environment that is ideal for cathode function. The cathode uses the water to make hydroxyls for the electrolyte. This is a closed space, so the only egress is through the permeable barrier into the anode side. The now concentrated and hydroxyl rich B stream flows into the anode side, where the anode is receiving fuel enriched fluid ideal for its function. The mixed fluid egresses through the porous anode bringing high concentration of fuel and hydroxyls to optimize its function. The cathode does not

- 25 -

experience much fuel, limiting crossover. The net flow is in the direction of the hydroxyl diffusion, speeding up mass transport.

In a different but similar permutation, the fuel, water electrolyte/etc mixture is passed through a means of constituent separation to relatively separate out at least the fuel. This means could be one or more of many such as distillation known to those familiar with chemistry. The fuel rich mixture may be directed relatively towards the anode, the water rich fluid may be directed relatively towards the cathode. This limits crossover reactions.

There may be included, in or relatively separated from the fuel and/or electrolyte, an oxygen carrying substance(s) such as, peroxides or artificial blood replacement/expanders to bring O2w where needed. This allows for a cathode with out an air interface layer for much higher kinetics.

The present inventions have been described herein in the context of various permutations and embodiments illustrated and/or described herein, the inventions may be formed or embodied in other specific fashions or forms without departing from the intention or spirit of these invention or this application. All above descriptions and diagrams are of an illustrative nature and should not be deemed as restrictive.

Appendix A

Problems specific to PEM type fuel cells

Hydrogen fueled PEM technology currently leads the industry. It has many important advantages, but is not without multiple weaknesses. The following is an in depth discussion of the challenges facing PEM technology.

The first problem with PEMs is, as above, they are too expensive from both a materials and manufacturing perspective. PEMs require platinum. Platinum is very rare and its supply is mainly restricted to the former USSR and South Africa. If we start mass-producing platinum containing devices, the supply/demand curve will shift, causing the already prohibitive price to rise. Additionally, platinum mining is very damaging to the environment. Ten tons of earth are moved for each ounce of recovered platinum. Platinum, as a catalyst, is also sensitive to poisoning compounds commonly found in most fuel stock.

To lower platinum requirements, PEMs use esoteric components such as nanoparticles. Again, this is expensive and not easily lent to mass production. Further, these advanced composites are sensitive to damage from the vibration that can be expected from some applications. Also, the electrodes have a high internal resistance that decreases efficiency. This necessitates the use of expensive, inefficient, and bulky field flow plates. In fact, a majority of stack volume and cost stems from field flow plates.

The membranous electrolytes are expensive and too sensitive to water balance and temperature issues.

PEMs are very susceptible to water balance problems and need to have a specific degree of water concentration at each part. If the parts get too dry or too wet they will not function. This problem is worsened because they operate in changing ambient humidity and encounter frequent temperature and load fluctuations. Furthermore, waste product water is formed at the cathode, which can flood it, and water is dragged from the anode drying it. This creates a cell that is essentially never functioning optimally, is quite sensitive to ambient and operating conditions, and requires additional water handling equipment that parasitizes the system's electricity. The water balance issues decrease efficiency in three ways. First uniformly optimal humidification is impossible to maintain, so the cell does not run at its best. Second, there is the additional manufacturing and maintenance costs of the necessary additional water balance equipment. Third is the parasitic energy loss from running that additional equipment.

Aside from water balance issues, the stack needs to maintain a delicately balanced interface of solid, liquid, and gas components, called the triple interface. Varying temperature, pressure, humidity, and shifting load conditions change this balance. Any perturbation of conditions slows or stops the energy production.

The PEM design suffers from many sources of efficiency loss. These include activation energy, internal resistance, and concentration losses. Resistance to the flow of ions in the electrolyte and resistance to the flow of electrons through the electrode materials create an internal resistance that drops actual voltage. Concentration loss occurs on a microscopic surface level. As the electrode consumes the reactant, product water is produced on the catalyst. The concentration of reactants near the catalyst becomes diluted by the product water, causing a loss of voltage potential. The current arts non flow-through electrode exacerbates this problem. The non-fuel substances

become trapped in relatively blind channels, excluding new reactants from penetrating the electrode to create more electricity.

Another important obstacle to widespread PEM commercialization is hydrogen. PEMs are not fuel flexible; they can only run on hydrogen. As discussed above, hydrogen is volatile, explosive, and expensive to store. It makes metals brittle and escapes trough microscopic cracks. Storage techniques are too bulky, expensive and/or risky. Further, hydrogen is a very non-dense gas. To get a useful amount of hydrogen in one place it has to be compacted under tremendous pressure, which increases the types and likelihood of potential mishaps. Cryogenically cooling it into a liquid uses up much of the energy stored in the hydrogen. The refrigeration has to be maintained; otherwise the liquid hydrogen evaporates in its closed tank creating tremendous pressure. Moreover, there is no adequate infrastructure for hydrogen storage and distribution.

The final barrier to PEM cells is also the least acknowledged. PEM design uses a membrane to separate the hydrogen from the oxygen. The membranes are paper thin and semipermeable. The gasses are hot, pressurized, and create caustic, reactive intermediary compounds that permeate the apparatus. Over time the membranes develop leaks that allow mixing of hot pressurized hydrogen and oxygen inside an electrically active device that makes sparks. It is potentially hazardous.

Even if all other cost and efficiency problems were solved, there are still significant challenges to address. PEM technology has enough advantages that it will capture a significant market share, but other technologies have equal or greater potential.

CATALYST PARTICLES

CARBON SUPPORT

PTFE/ELECTROLYTE BINDER

ELECTROLYTE MEMBRANE

CARBON FIBER FOR SUPPORT

CATALYST-CARBON COMPLEX THAT DOES NOT TOUCH ELECTROLYTE

ANODE

CATHODE

MEMBRANE
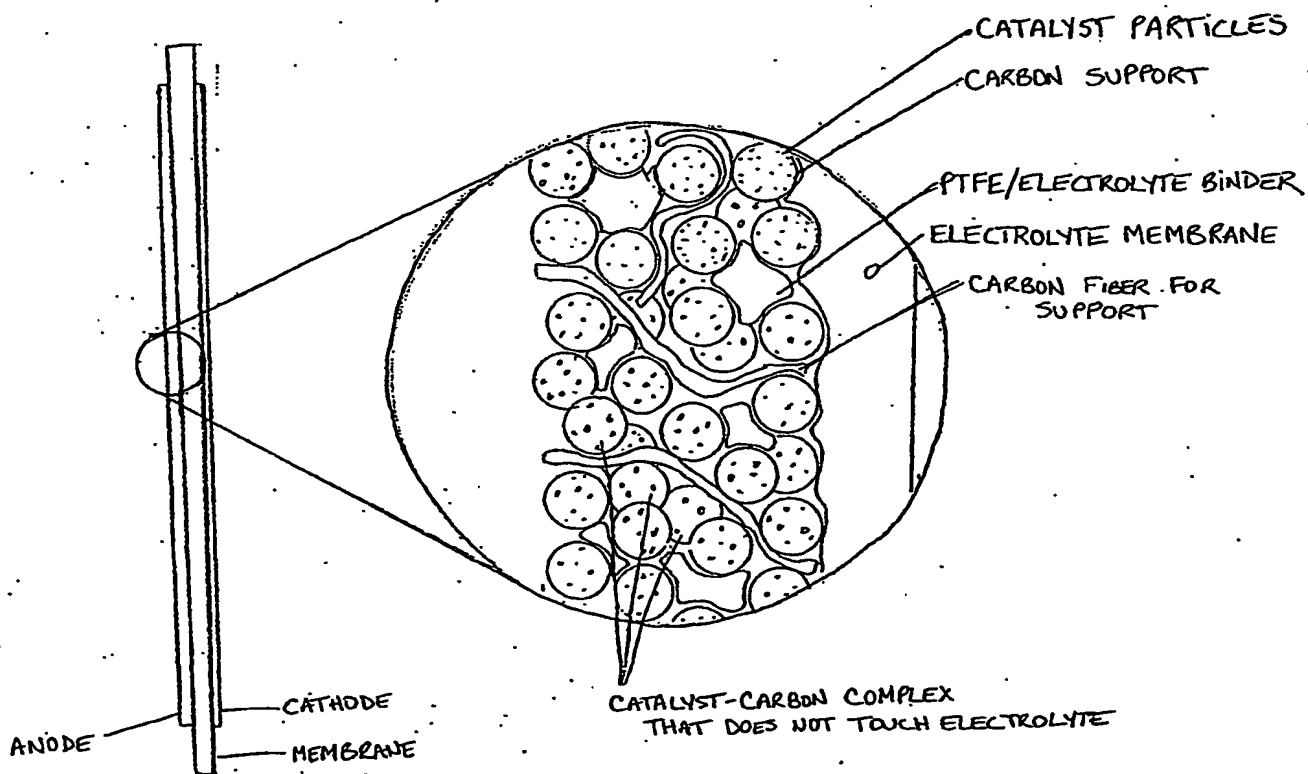
FIGURE A: SIDE AND EXPANDED VIEW OF CURRENT ART ELECTRODE AND ELECTROLYTE ASSEMBLY

Figure A.

FIGURE 1: DIAGRAMMATIC REPRESENTATION OF THE IMPROVED ANODE WITH MAGNIFIED VIEWS.

FIGURE 1A

Anode Flat plate
Side view
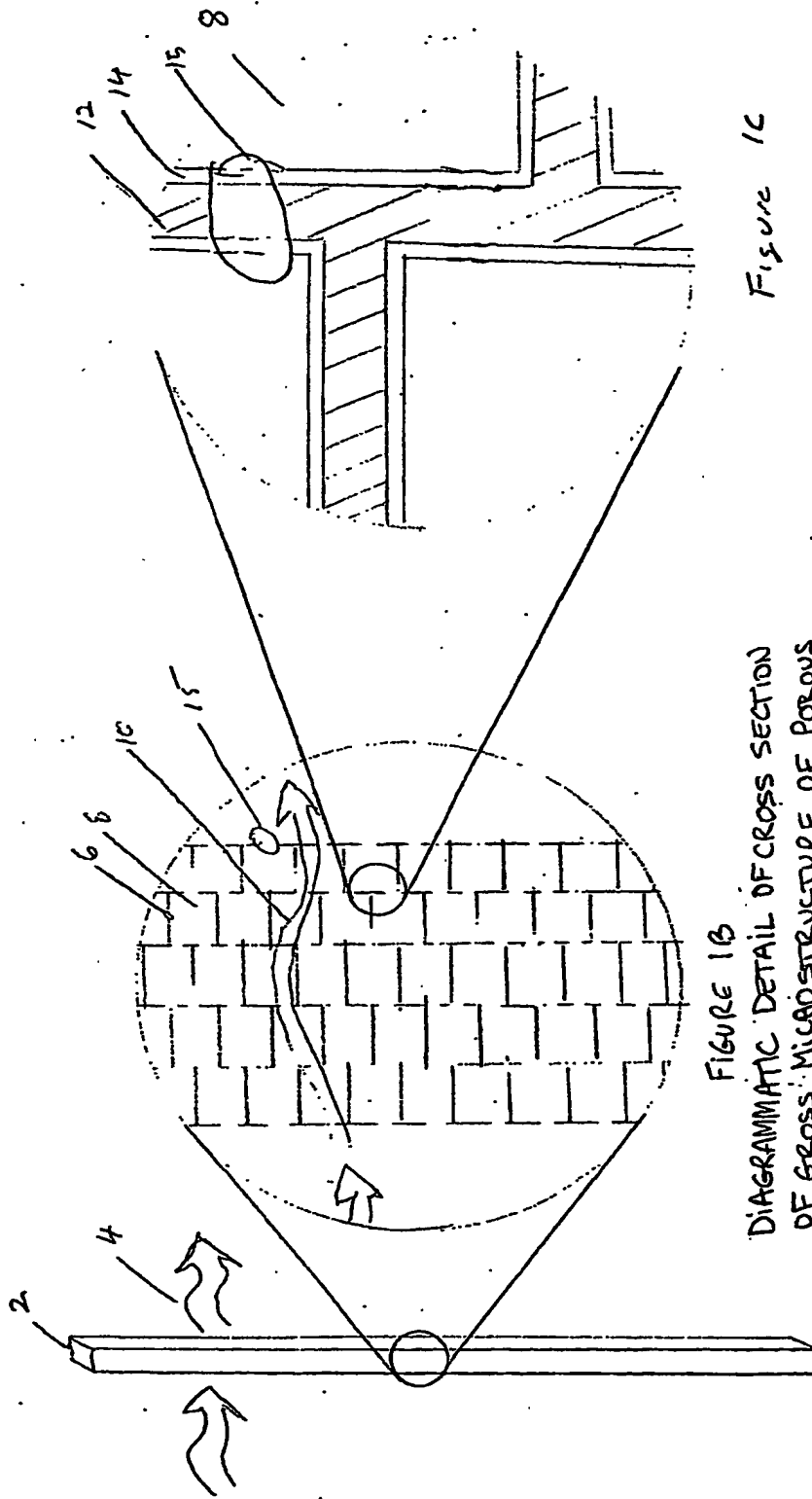
FIGURE 1B

DIAGRAMMATIC DETAIL OF CROSS SECTION
OF GROSS MICROSTRUCTURE OF POROUS
FLOW THROUGH ANODE.

Figure 1c

Detail of fine microstructure

1C (a)

1C (b)

1C (c)

1C(d)
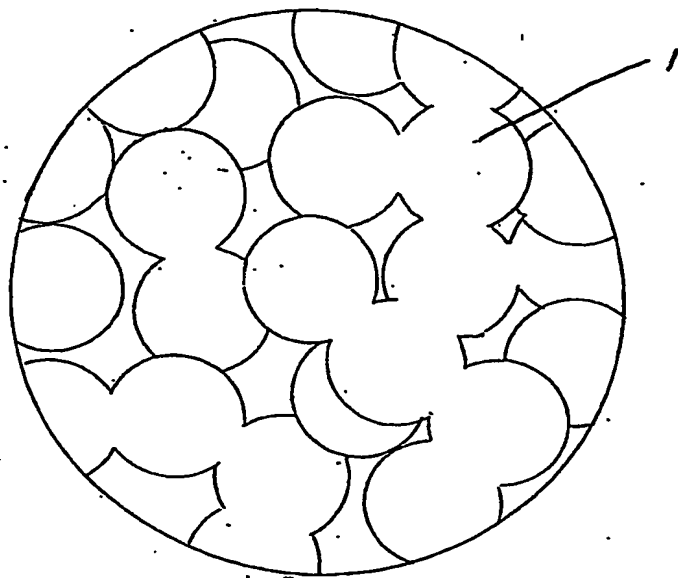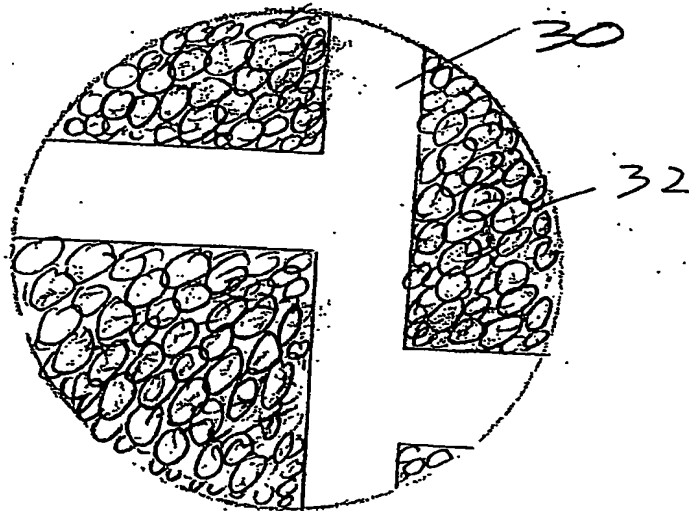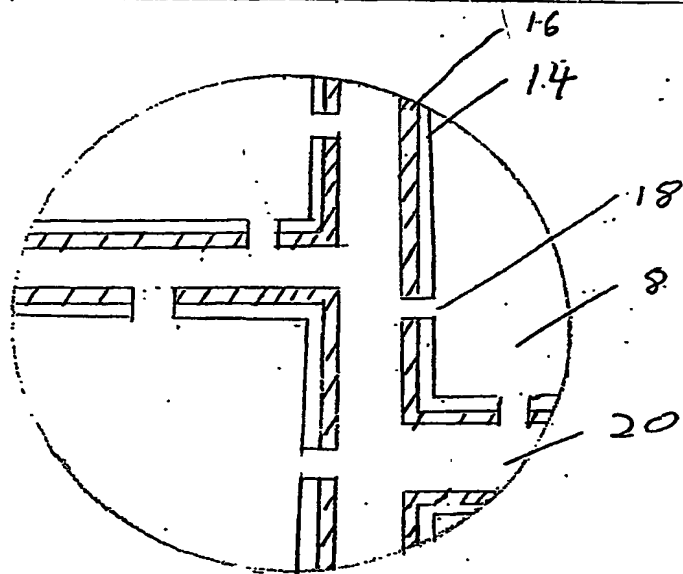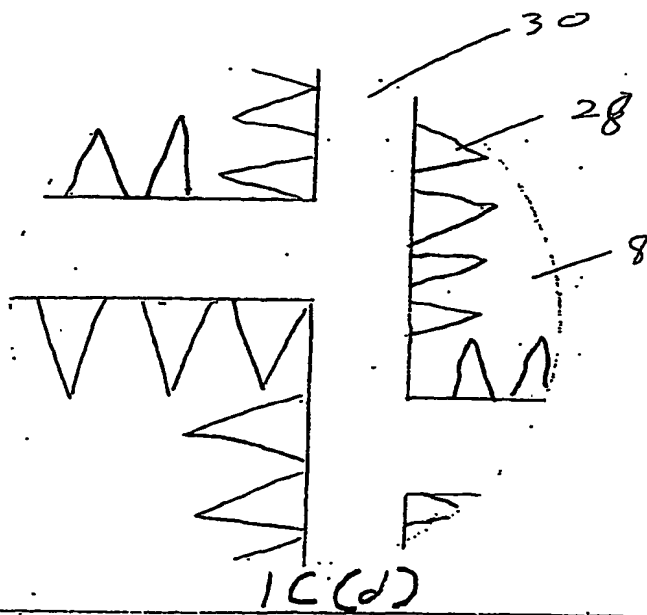
Figure 1C(e)

Figure 1C(f)
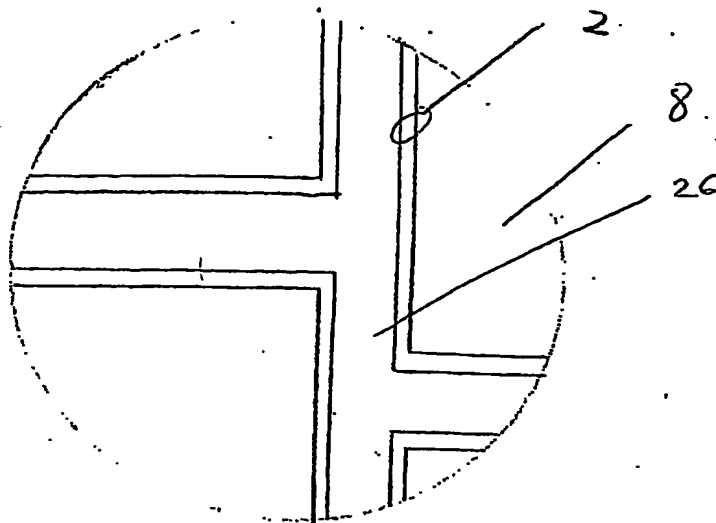
Figure 1C(g)
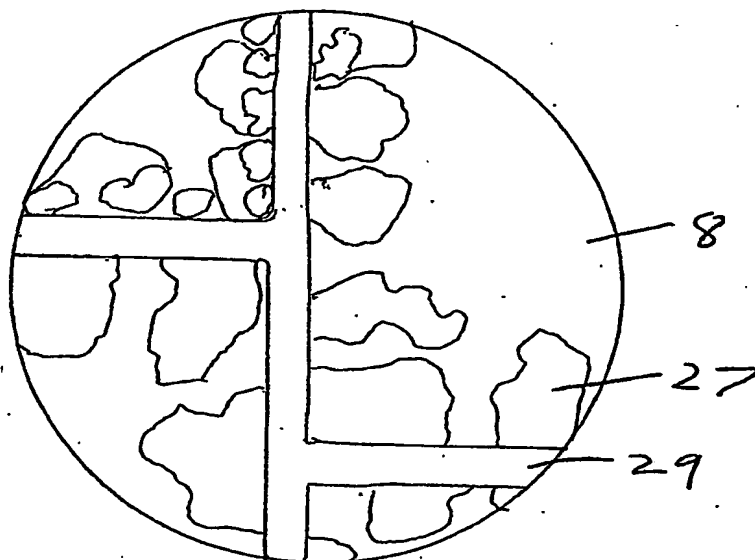
1C(h)

Figure 2B Side view of
Anode with Iradient surface area
and pore size

42 44 46

Figure 2A Side view diagramatic
of Anode with high flow core

36

38

40

38

4 - Diagrammatic representation of a fuel cell design with fuel ...

126

124

116

114

104

120

118

128

130

Figure 6 Sketch of manifolds placement relative to the stack case.

136
138
140 142
132 134 176 136
132 134 135
132

Figure 7A Side view rarified core anode surrounded by two cathodes

132
136
144
132

134 134
132

Figure 7b Side view of a through anode surrounded by two cathodes.

146
136
132

Figure 7c Side view of a flow 7 c Side view of a single cathode paired with a more massive anode.

Figure 7c

flow by cathode

flow through anode

Flow

PUMP

148

150

155

157

160

152

151

154

Figure 8. Diagram of separated anodes and cathodes permutation demonstrating differential

160
162
164 168
170
160
162
190
188
170
172
180
178
174
175
172
176

— f separated anodes and cathodes

192 Stack

196

194 Fan

198 G

206

204

202

200

199

air

H_2O

electrolyte